



Biomass torrefaction under different oxygen concentrations and its effect on the composition of the solid by-product

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ABSTRACT

Torrefaction is a thermal treatment used to improve the properties of biomass in relation to thermo-chemical processing techniques for energy generation. It is a thermo-chemical treatment method primarily characterized by an operating temperature within the 200–300 °C range. It is carried out under conditions of atmospheric pressure and in the presence of a minimum amount of oxygen in order to avoid spontaneous combustion. The aim of this study was to evaluate the combined effect of the temperature (240 and 280 °C) and oxygen concentration (2, 6, 10 and 21%) on the physical and chemical properties of large particles of *Eucalyptus grandis*. A statistical analysis was carried out. The different oxygen concentrations did not significantly affect the composition of the solid by-product for low temperatures. At 280 °C, the high oxygen concentration affected some of the properties studied.

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1. Introduction

The global problems associated with the intensive use of fossil fuels have increased interest in the use of renewable fuels worldwide, mainly in countries like Brazil, where biomass is widely available at low cost. However, a pre-treatment process is required to convert biomass into a hydrophobic solid product with an increased energy density [1]. One way to achieve that goal is to apply torrefaction, which is considered as a biomass feedstock pre-treatment, particularly for thermal conversion. It is gaining attention as an important pre-processing step for improving biomass quality in terms of physical properties and chemical composition [2,3]. Torrefaction involves the slow heating of biomass in an inert environment or reduced O₂ content to a maximum temperature of approximately 300 °C. Torrefaction can also be defined as a group of products resulting from the partially controlled and isothermal pyrolysis of biomass occurring in a temperature range of 200–280 °C [4,5]. The yields and properties of torrefaction by-products are influenced by several parameters, including biomass composition, particle size, processing temperature and time, heating rate and the composition of the working atmosphere [6,7]. Much work has been done to study how these operating parameters influence torrefaction [8,9], but there still remains a need to study the influence of different oxygen concentrations on the thermal reactivity of large biomass particles during torrefaction, as well

as their effect on the physical and chemical properties of torrefied biomass.

The thermal decomposition of lignocellulosic materials involves a complex series of chemical reactions and heat and mass transfer processes [10–12]. An oxidizing atmosphere can promote the oxidative degradation of the material and the subsequent oxidation of the volatile matter released during such degradation, in addition to promoting the combustion of the char residue. Studies to evaluate the thermal behaviour of biomass in both oxidizing and inert atmospheres have been carried out by several authors [13,14]. Most of them showed that when oxygen is present, the thermal reactivity of biomass (especially cellulose) is greatly enhanced due to the acceleration of mass loss in the first stage of pyrolysis. Analysing the influence of the initial solid weight and the sample shape on solid conversion for different oxygen concentrations, Bilbao [15] proposed a simple model. He showed that the influence of oxygen concentrations on mass loss depends on the weight of the sample and the temperature at which the process occurs. More recently, Shen and his co-authors [16] used a DAEM method and global kinetic model in both inert and oxidative atmospheres to examine the mechanisms involved in the thermal decomposition of wood. The apparent activation energy of pyrolysis and combustion varied linearly with oxygen concentration [17]. However, these studies were carried out at high temperatures using small samples. For temperature lower to 250 °C, the mass losses rates of wood were similar. Thus, it is important to evaluate the effect of different oxygen concentrations in the working atmosphere using larger samples, closer to the true conditions of use, and at the low temperatures of torrefaction process.

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This study investigated the thermal reactivity of *Eucalyptus grandis* during torrefaction under different oxygen concentrations by examining the relationship between mass loss and the physical and chemical properties of the solid by-product.

2. Material and methods

2.1. Materials

The raw material was *Eucalyptus grandis* wood obtained from a 31-year-old plantation at an experimental station administered by the Forestry Science Department of the University of São Paulo/ESALQ, in the municipality of Piracicaba (Brazil) [6]. Three trees were felled and planks were cut to make samples, each measuring 10 mm × 40 mm × 80 mm, respectively the thickness, the width and the length. The samples were previously dried to a constant weight at 105 °C. The proximate and ultimate analyses and the gross calorific value of *Eucalyptus grandis* wood are shown in Table 1.

2.2. Torrefaction device

The experimental system (Fig. 1) consists of a precisely controlled temperature batch reactor. A programmable PID (proportional-integral-derivative) controller was used to control the temperatures and heating rate of the reactor thanks to three thermocouples: one in the base (near the electric heater), one inserted through the lid of the reactor (at the top of the reactor) and the last one inside the sample to monitor its temperature. A nitrogen source is used to control the oxygen content; the oxygen, carbon monoxide and carbon dioxide contents inside the reactor are measured with a gas analyser. Two samples were tested in each trial run, one coupled to a precision balance to monitor mass loss (sample 2) and another with a thermocouple to monitor the internal temperature (sample 1).

The temperature of the reactor was raised to the selected temperature (240 or 280 °C) by a linear heating rate of 4 °C min⁻¹, and held for 60 min at that temperature. Nitrogen was introduced into the system in order to perform experiments with oxygen percentages in the atmosphere of 2, 6, 10 and 21%. The chosen oxygen rate was maintained during sample cooling. The system provided continuous acquisition of the temperature, oxygen level and sample mass. The data were recorded every minute during thermal decomposition. All experiments were performed twice.

The thermal decomposition of wood was also evaluated in terms of conversion rate, which was calculated over time for all treatments. The conversion rate, α , was defined as:

$$\alpha = \frac{M_0 - M_t}{M_0}, \quad (1)$$

where M_0 is the initial solid mass (dry basis) and M_t is the solid mass at time t .

2.3. Solid analysis

Proximate and ultimate analyses were performed on torrefied samples, as well as the gross calorific value. Proximate analyses (volatile matter, ash and fixed carbon contents) were conducted according to the procedure of the Brazilian Association of Technical Standards – ABNT NBR 8112 (ABNT, 1986). The ultimate analysis (C, H, N, O contents) was carried out with a Vario Macro CHN elemental analyser, according to the European procedure XP CEN/TS 15104. The oxygen content was calculated by difference. The gross calorific value was measured in a Parr 6200 isoperibol oxygen bomb calorimeter in accordance with the European procedure XP CEN/TS 14918. The lignin content of the torrefied samples was

measured according to the standard method NREL LAP-003, for acid-insoluble lignin, and NREL LAP-004 for acid-soluble lignin. All the analytical characterizations were carried out on extractive-free milled samples. The solvent for extraction was ethanol–toluene.

2.4. Statistical analysis

Sixteen assays were conducted, corresponding to 8 treatments and two replicates. We used a modular statistical software, XLSTAT (addinssoft), to enhance the analytical capabilities of Excel. It handles models relating one or more continuous dependent variables to one or more independent variables. Ten variables in response to the experiments were analysed and discussed: the mass loss ($W_t\%$), the fixed carbon content (FC%), the volatile matter content (VM%), the ash content (Ash%), the carbon content (C%), the hydrogen content (H%), the nitrogen content (N%), the oxygen content (O%), the lignin content (L%) and the gross calorific value (GCV). The values for the oxygen concentration in the reactor ($O_2\%$) and the temperature (T) parameters were defined in accordance with earlier work [9,18]. The general model for variance analysis was that described by the following equation:

$$Y_{ij} = \beta_0 + [O_{2i} + T_j + (O_2 \times T)_{ij}] + \varepsilon_{ij} \quad (2)$$

where Y_{ij} is the value observed for the dependent variable for observation ij , O_2 is the oxygen concentration in the reactor, T the temperature and ε_{ij} is the error of the model. β_0 is a constant.

3. Results and discussion

3.1. Proximate and ultimate analyses

The results of the ultimate and proximate analyses and gross calorific value of all the torrefied samples, as well as the final conversion and summary statistics for the experimental factorial design performed, are shown in Table 1. We carried out an analysis of variance (ANOVA) of the means obtained, taking into account possible interactions between the two explanatory variables: oxygen rate and temperature.

The results show that there were globally no significant differences between the means obtained with the different oxygen rates, whereas the temperature significantly impacted on mass loss, lignin rate and carbon and oxygen rates. It was found that the volatile matter rate displayed a significant difference between 240 °C/21% and 280 °C/6% with 80.59 and 71.20% respectively. Whilst the GCV was greatly linked to the lignin content, we found that, despite a significant increase in the relative lignin content due to the cellulose and hemicelluloses degradation [18], the gross calorific value showed a tendency to increase, though not significantly. These observations are only valid in the case where we used the model with level 2 interactions ($O_2 \times T$). We modelled these means without taking into account interactions between the explanatory variables; the results confirmed the absence of any significant impact of the oxygen concentration in the reactor whilst the temperature had a significant impact on 8 of the 10 variables observed. These observations corroborated several studies focusing on the effects of torrefaction parameters on end-product quality [19].

From the model described previously (Eq. (2)), we performed type III sum of squares to analyse which parameters significantly interfered ($\alpha = 0.05$) with the ten response variables, along with the effect of second order interactions on the quality of the torrefied biomass produced. Of the parameters studied, the temperature was the factor with the greatest impact on 8 of the 10 response variables. The oxygen content in the reactor and the second order

Table 1
Classification by Tukey's test of averaged results for the 10 response variables considering 2 replicates per treatment. For each group, the means with the same letter were not significantly different at 5% ($\alpha = 0.05$). V.M.: volatile matter; F.C.: fixed carbon; CGV: gross calorific value; S.D.: Standard deviation; C.V.: coefficient of variation; R^2 : coefficient of determination. Contr.: untreated samples.

Torrefaction treatments		Proximate analysis (%)			Ultimate analysis (%)						
T (°C)	O ₂ (%)	V.M.	F.C.	Ash	C	H	N	O	L (%)	GCV (J/g)	Wt (%)
240	2	79.56ab	20.37a	0.07 a	54.26a	5.54a	0.04a	40.17a	45.03a	20854a	91.35a
240	6	79.36ab	20.58a	0.06 a	54.33a	5.51a	0.09a	40.08a	43.64a	21020a	92.86a
240	10	77.46ab	22.44a	0.11 a	54.41a	5.45abc	0.09a	40.05a	43.23a	21068a	92.32a
240	21	80.59a	19.40a	0.04 a	54.02a	5.47ab	0.10a	40.41a	43.48a	20999a	91.97a
280	2	75.60ab	24.13a	0.27 a	57.22b	5.36abc	0.10a	37.32b	53.91ab	22223a	81.53b
280	6	71.20b	28.70a	0.10 a	58.21b	5.17abc	0.06a	36.55b	58.46b	22239a	80.61b
280	10	73.10ab	26.80a	0.10 a	58.63b	5.07bc	0.06a	36.24b	60.56b	23404a	79.79b
280	21	73.14ab	26.70a	0.17a	58.47b	5.05c	0.06a	36.42b	60.06b	22497a	78.53b
Contr.	–	80.15	19.56	0.29	51.2	5.8	0.05	42.95	35.60	18030	100
S.D.		0.1	3.8	3.8	2.09	0.21	0.04	1.89	7.98	934	6.35
C.V.		0.84	0.05	0.16	0.04	0.04	0.47	0.05	0.15	0.04	0.07
R ²		0.79	0.78	0.53	0.96	0.87	0.35	0.97	0.93	0.99	0.97

interaction between O₂ and T(O₂ × T) did not significantly influence the variables (Table 2).

3.2. Effects of oxygen concentration on thermal reactivity

Fig. 2 shows the effect of the oxygen concentration on the conversion rate for both temperatures 240 and 280 °C. We found conversion rates that were 2.5 times greater for the extreme temperatures for a given reaction time; these results were confirmed by earlier work [18,20,21]. For 240 °C, the conversion rate values varied from 0.07 to 0.09, whilst at 280 °C, two groups of curves were found with values of between 0.17 and 0.24. For each treatment, the tendency showed an increase in conversion rate with oxygen concentration; results are similar than those obtained in thermogravimetric analyses (TGA) [16,17]. That increase was more visible at 280 °C with a conversion rate α equal to 0.17, 0.18, 0.20 and 0.24 for 2, 6, 10 and 21% of oxygen, respectively. Similar assays focusing on the dynamic pyrolysis of coniferous sawdust exhibited mean values of between 0.20 and 0.40 for oxygen concentrations ranging from 0 to 21% [15]. These differences seem to be primarily due to the size of the sample and to operating conditions, as the author worked with dynamic heating. Indeed, some work has shown the role of sample thickness in heat and mass transfers and the presence

Table 2
Analysis of variance of the temperature (T) and the oxygen content (O₂) parameters, along with their first and second order interactions for the ten response variables. * = significant; ns = not significant at 5%. The p-values are in italics.

Response variable	T	O ₂	T × O ₂
Wt (%)	*	ns	ns
	<i><0.0001</i>	<i>0.527</i>	<i>0.383</i>
Ash (%)	ns	ns	ns
	<i>0.086</i>	<i>0.557</i>	<i>0.421</i>
V.M. (%)	*	ns	ns
	<i><0.0001</i>	<i>0.453</i>	<i>0.519</i>
F.C. (%)	*	ns	ns
	<i><0.0001</i>	<i>0.46</i>	<i>0.541</i>
N (%)	ns	ns	ns
	<i>0.664</i>	<i>0.976</i>	<i>0.328</i>
C (%)	*	ns	ns
	<i><0.0001</i>	<i>0.332</i>	<i>0.335</i>
H (%)	*	ns	ns
	<i><0.0001</i>	<i>0.098</i>	<i>0.427</i>
O (%)	*	ns	ns
	<i><0.0001</i>	<i>0.356</i>	<i>0.358</i>
Lignin (%)	*	ns	ns
	<i><0.0001</i>	<i>0.631</i>	<i>0.229</i>
GCV (J/g)	*	ns	ns
	<i>0.039</i>	<i>0.228</i>	<i>0.28</i>

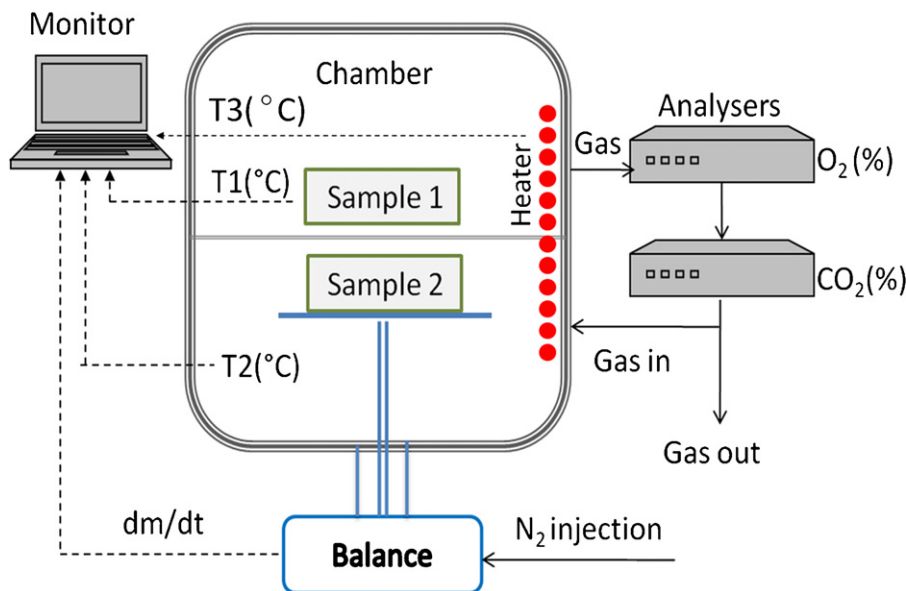


Fig. 1. Torrefaction schema with balance and analysers (O₂ and CO/CO₂). T1 and T2 are the thermocouples respectively in the sample and in the chamber and T3 controls the electrical heater.

Table 3

Maximum rates of mass loss, internal temperatures of samples and reactivity and conversion rate obtained throughout the process duration. For each group, the means with the same letter were not significantly different at a probability of 5% with regard to Tukey's test.

Temperature (°C)	Oxygen concentration (%)	Maximum rate of mass loss (g/min)	Peak internal temperature (°C)	Reactivity (g/min/°C)	Conversion rate, α
240	2	0.06	224.3	0.03	0.040c
	6	0.05	235.7	0.02	0.041c
	10	0.06	236.9	0.03	0.044c
	21	0.12	229.8	0.05	0.042c
280	2	0.36	280.9	0.13	0.08b
	6	0.39	273.0	0.14	0.089b
	10	0.31	281.2	0.11	0.091b
	21	0.36	280.8	0.13	0.114a

of exothermal reactions [22,23]. For instance, the sample temperature increased, becoming higher than that of the reactor, speeding up the oxidation rate of the remaining material [24,25]. In our case, as the treatment duration was limited to 60 min, these thermal runaway phenomena were only partially found, whatever the oxygen concentration [22]. Only the value obtained at 280 °C and 21% of oxygen appeared significantly different from the values obtained at the same temperature for 2, 6 and 10% of oxygen (Table 3).

The effect of the oxygen concentration combined with the different treatment temperatures was also assessed from the mass loss and thermal reactivity of the samples. Fig. 3 shows the mass loss trend as a function of time for each of the oxygen concentrations, along with the differential thermal gravimetry expressed in g/min calculated from the derivative of the mass loss curves during time. In all cases, the tendency revealed an increase in differential thermal gravimetry with the increase in oxygen concentration in the reactor. For 240 °C and 280 °C, the mass loss percentages rose

from 7 to 9% and 17 to 22% respectively for the highest oxygen concentrations. Some studies have shown that for a treatment at 280 °C for 5 h, mass loss can exceed 35% [20].

However, the scale of this increase differed for each temperature. For the two treatments, we found a dm/dt peak between 70 and 80 min of treatment. These peaks were more marked at 280 °C, whatever the oxygen concentration. According to Bilbao, that peak would seem to correspond mainly to the thermal and oxidative degradation of the solid [15]. For the high oxygen contents, this maximum was obtained for temperature values ranging between 320 and 327 °C, i.e. 40 °C above our treatment temperatures. For the lower temperatures, mass losses from the treated samples did not display any significant difference. These results were found by Fang [17] who assessed the effect of oxygen concentration on mass loss from wood samples treated at 250 °C and concluded that up to 250 °C, the mass loss curves are similar.

As proposed by Ghetti [13], the reactivity of the material can be deduced from the degradation peaks shown in Fig. 3. He suggested that the mass loss rate peak (r) is directly proportional to reactivity R , with the corresponding temperature T being inversely proportional to that reactivity. On that basis, we calculated the reactivity for all the treatments using the formula: $R = 100(r/T)$. Table 3 presents the maximum rates of mass loss and the internal temperatures at which these rates were determined, as well as the reactivity calculated during torrefaction. We found that the reactivity values for the samples were 2.6–4.3 times higher for the samples treated at 280 °C than those treated at 240 °C. Statistically, the results obtained did not reveal any differences, but in absolute terms the lowest reactivity values could be seen for the lowest temperatures, which can be explained by a breakdown of hemicelluloses, which are more reactive at low temperatures [12].

Using Table 3, we carried out a multiple regression with the maximum rates of mass loss as quantitative explanatory variables and reactivity as the response variable. The number of degrees of freedom for the chosen model was 6 and the determination coefficient was 0.998. The p -value was <0.0001, so the lower the probability, the greater the contribution of the variable to the model. The results showed that the specific maximum weight loss rate can be used as a commonality parameter to evaluate and distinguish the reactivity of the treated biomass [13,26,27]. The equation of the model is shown in Fig. 4. The chart displayed shows the observed values, the regression line and both types of confidence interval around the predictions.

3.3. Van Kreevelen classification

The change in composition from biomass to torrefied biomass can be illustrated using a diagram developed by Van Kreevelen. From a recent work, it was found that the carbon content of the torrefied wood increased significantly when increase the temperature and

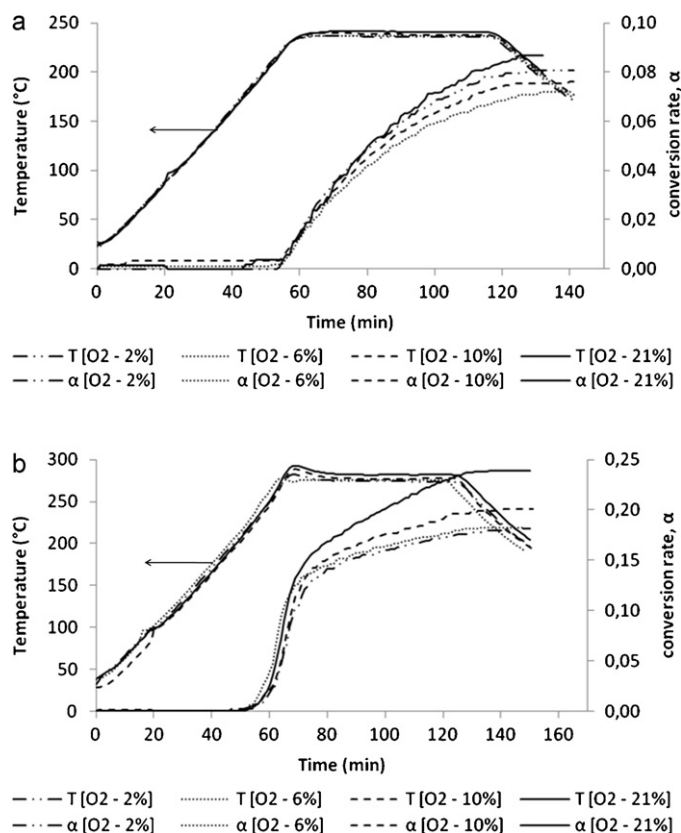


Fig. 2. Conversion rate due to torrefaction according to oxygen concentration and internal temperature of samples (heating rate: 4 °C min⁻¹): (a) 240 °C (b) 280 °C.

Table 4

Classification by Tukey's test of the averaged results for elemental composition of torrefied eucalyptus considering 2 replicates per treatment. For each group, the means with the same letter were not significantly different at 5%.

Torrefaction treatment		H/C (average)	O/C (average)
240 °C	O ₂ – 2%	1.225a	0.560a
	O ₂ – 6%	1.220a	0.555a
	O ₂ – 21%	1.215a	0.550a
	O ₂ – 10%	1.205a	0.550a
	O ₂ – 2%	1.125ab	0.490b
280 °C	O ₂ – 6%	1.070b	0.475b
	O ₂ – 10%	1.040b	0.465b
	O ₂ – 21%	1.040b	0.465b

holding time during the torrefaction [28]. Fig. 5 shows the change in H/C and O/C atomic ratios of torrefied biomass composition for each temperature and oxygen concentration. We found two groups linked to temperature. Due to the removal of water and carbon dioxide, the composition of the torrefied product had a lower O/C and H/C ratio than untreated biomass. In relation with the oxygen concentration, the tendency was towards a reduction in the O/C and H/C ratios, with that tendency being more marked for the severest thermal treatment. These observations confirmed our earlier results, even though, statistically, these differences were not significant (Table 4).

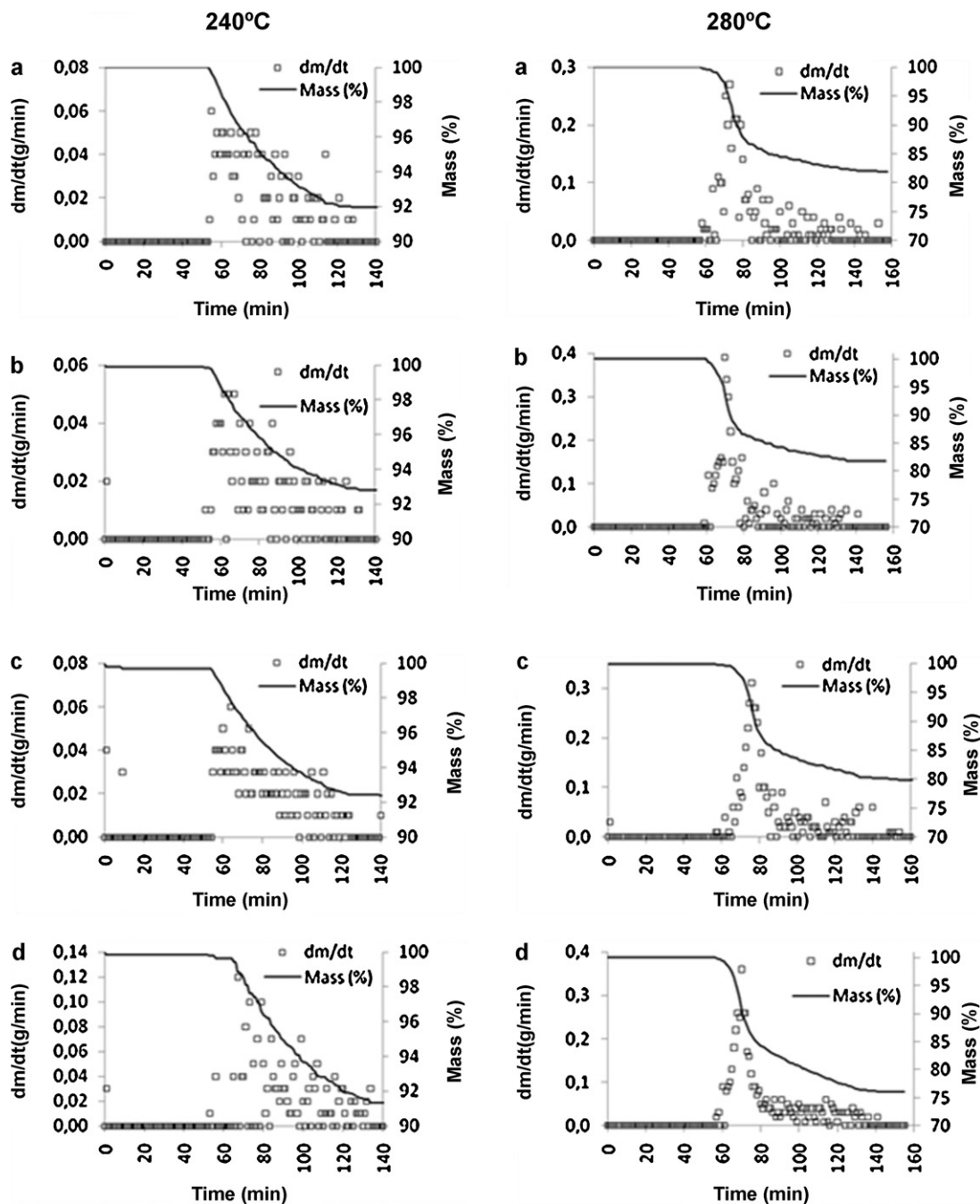


Fig. 3. Effect of O₂ concentration on mass loss and dTG for *Eucalyptus grandis* at 240 °C and 280 °C (heating rate: 4 °C min⁻¹): (a) O₂ – 2%, (b) O₂ – 6%, (c) O₂ – 10%, (d) O₂ – 21%.

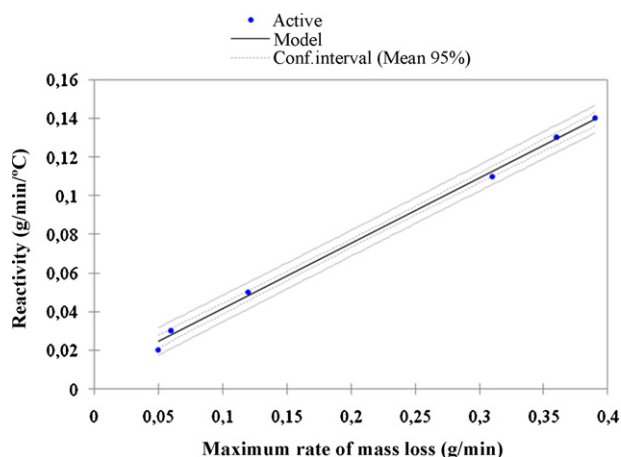


Fig. 4. Regression of reactivity ($\text{g/min}/^{\circ}\text{C}$) by maximum rate of mass loss (g/min) ($R^2=0.998$). The equation is: $\text{Reactivity} = 7.75 \times 10^{-3} + 0.33 \times \text{maximum rate of mass loss}$.

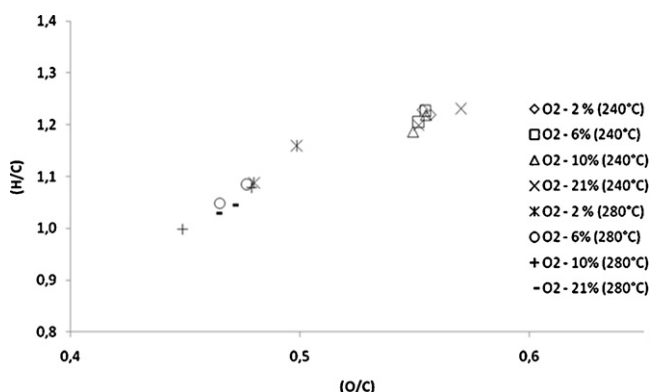


Fig. 5. Composition of torrefied eucalyptus wood (obtained at temperatures of 240 and 280 °C and oxygen concentrations from 2 to 21%) in the van Krevelen diagram.

4. Conclusions

The originality of this work concerned the torrefaction of large pieces of wood under different oxygen concentrations and temperatures. From the foregoing, some meaningful conclusions can be drawn: The mass losses were very similar when the temperature was under 240 °C whatever the oxygen concentration. At 280 °C, the tendency was more marked, but was only significant for high oxygen contents (21%). Although the parametric study did not show influence of oxygen content on torrefied biomass composition, variations in oxygen concentrations in the reactor during torrefaction influence very slightly the chemical composition of the wood, by decreasing the H/C and O/C ratios when oxygen content increases. Nature of gaseous and condensable species released during torrefaction is therefore affected by the oxygen content inside the reactor. These results will be studied in future work. The results showed that the specific maximum weight loss rate can be used as a commonality parameter to evaluate and determine the reactivity of torrefied biomass. The statistical study showed the increase in oxygen content in the reactor did not significantly affect the reactivity of the wood and its chemical composition for low temperature, we suggest the use of an inert atmosphere for temperatures up to 280 °C to avoid combustion of volatile products formed during wood degradation. The exothermic reactions associated with this combustion could increase temperature locally in the wood resulting in a heterogeneous heat treatment [17]. Other studies are currently under way to determine more precisely the combined

effect of the oxygen concentration and heating temperature on large pieces of wood.

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